

SUPPORTING INFORMATION

Cuboctahedron-based indium-organic frameworks for gas sorption and selective cation exchange**

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S1. Materials and Methods

1.1. Materials and Instruments.

Reactions were carried out in 25 ml Teflon-lined autoclave under autogenous pressure. All the reactants are of reagent-grade quality and used as commercially purchased without further purification.

The power X-ray diffraction patterns (PXRD) were collected by a Bruker D8 Advance using Cu K α radiation ($\lambda = 0.154$ nm).

Single gas adsorption measurements were performed in the Accelerated Surface Area and Porosimetry 2020 (ASAP2020, the Fujian Institute of Research on the Structure of Matter (CAS)) System, in which **InOF-9** was determined in a clean ultra high vacuum system and the N₂ sorption measurement was performed at 77 K.

Elemental analyses for C, H, N were carried out on a German Elementary Vario EL III instrument.

Thermogravimetric analyses were recorded on a NETZSCH STA 449C unit at a heating rate of 10 °C·min⁻¹ under flowing nitrogen atmosphere.

Supercritical CO₂ activation is done in a Tousimis Samdri-PVT-3D instrument (the Fujian Institute of Research on the Structure of Matter (CAS) from Tousimis Research Cooperation (USA).

Scanning transmission electron microscopy (STEM) and energy dispersive X-ray spectroscopy (EDS) analyses were carried out under JEOL JEM-2100F microscope operating at an accelerating voltage of 200 kV.

Fluorescent spectra were measured on an Edinburgh Instruments analyzer model FLS920 with 450W xenon light.

1.2. Synthesis of [Me₂NH₂]₃[In₃(BTB)₄]•2DMF•2DMA•28H₂O (**InOF-9**)

A mixture of In(NO₃)₃ (0.10 mmol, 33 mg) and H₃BTB (0.10 mmol, 44 mg, H₃BTB = 1,3,5-tris(4-carboxyphenyl)benzene) in the mixing solvent of N,N'-Dimethylformamide (DMF) and N,N'-Dimethylacetamide (DMA) was sealed in a 25 ml autoclave, which was heated at 120 °C for four days, and cooled gradually to room

temperature in another day. As for the charge equilibrium, the DMA and/or DMF solvent molecules turn out to be decomposed into disordered Me_2NH_2^+ cations during the solvothermal reaction. After washed by fresh acetonitrile, the light yellow crystals were obtained in *ca.* ~50% yield based on the H_3BTB ligand. Elemental analysis was calculated for **InOF-9**: C, C, 50.22%; H, 6.06%; N, 3.20%. Found: C, 49.77%; H, 5.52%; N, 2.99%. The phase purity of the sample is confirmed by PXRD (Figure S4). Moreover, the as-synthesized crystals and the MB-trapped **InOF-9** sample (**MB@InOF-9**) has also been confirmed by EDS and the elemental mapping, respectively (Figure S7 and S8).

1.3. Synthesis of $[\text{Cu}_2(\text{IPA})_2]\cdot\text{Guest}$ (**Cu-IPA**)

A mixture of $\text{Cu}(\text{NO}_3)_2$ (0.10 mmol, 20 mg) and H_2IPA (0.10 mmol, 17 mg, H_2IPA = isophthalic acid) in the solvent of $\text{N,N}'$ -Dimethylformamide (DMF) was sealed in a 25 ml glass vial, which was heated at 85 °C for 5 days and cooled gradually to room temperature. Blue truncated-octahedral crystals were formed, which were washed with 3×10 mL of DMF, 40% based on H_2IPA ligand). The phase purity of the sample is also confirmed by PXRD (Figure S4).

1.4. Single-Crystal X-ray Crystallography

The structure data of **InOF-9** were collected on a SuperNova, Dual, Cu at zero, Atlas diffractometer. The crystal was kept at 100 K during data collection. By Using Olex2,^{S1} the structure was solved with the ShelXS^{S2} structure solution program using Direct Methods and refined with the ShelXL^{S3} refinement package using Least Squares minimisation. Crystallographic data and structure refinement parameters for this single crystal are listed in Table S1 below. In the meantime, we have also applied PLATON/SQUEEZE^{S4} to calculate the contribution to the diffraction from the solvent region and thereby produced a set of solvent-free diffraction intensities. The final formulae were calculated from the SQUEEZE results combined with elemental analysis data and TGA data. More details on the crystallographic studies as well as atomic displacement parameters are given in Supporting Information as CIF files.

Crystallographic data for the structure reported in this paper has been deposited. The following crystal structure has been deposited at the Cambridge Crystallographic Data Centre and allocated the deposition number (CCDC No.) 1472284. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif.

1.5. Supercritical Carbon Dioxide Drying^{S5}

First of all, as-obtained single crystals are evacuated with supercritical CO₂ in a Tousimis Samdri-PVT-3D instrument. Prior to the activation process, the as-synthesized DMF/DMA solvated **InOF-9** samples are soaked in pure acetonitrile solvent (MeCN), and refreshing the soaking solution every day for 5 days, in order to fully exchange the occluded solvent for MeCN. After the completed MeCN-exchange process, the MeCN-solvated samples are immediately placed inside the pressure vessel and the MeCN is exchanged with liquid CO₂ by opening the “FILL” button over a period of 3 hours, in which the CO₂ (liquid) is vented from 1100 psi to 1000 psi by very slowly unlocking the “BLEED” button for 5 minutes each 30 minutes. And then close the “BLEED” button and the chamber pressure return to 1100 psi, please notice the chamber temperature by adjusting the upper-left “COOL” button as well. After 3 hours of repeatedly venting and soaking with CO₂ (liquid) the chamber is sealed and the temperature is raised to 40 °C.

This would bring the chamber pressure to around 1300 psi above the critical point of CO₂. The chamber is then held above the critical point for another 3 hours at which point the chamber is slowly vented overnight (12 hours). Then the dried samples are quickly transported into an adsorption tube in the glovebox. The PXRD patterns of supercritical CO₂-exchanged **InOF-9** samples confirm that it retains the highly crystallinity and then are tested for nitrogen adsorption soon (Figure S4).

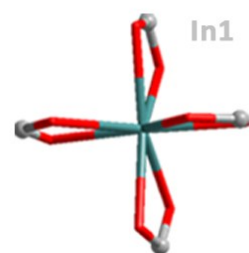
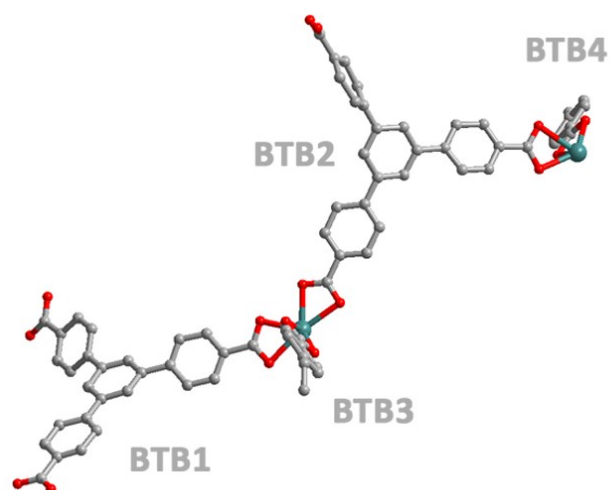
Table S1. Summary of Crystal Data and Refinement Results

Items	InOF-9
formula	$C_{72}H_{40}In_2O_{16}$
M	1390.68
crystal system	Trigonal
space group	$R\bar{3}$ (#. 148)
a (Å)	44.874(4)
b (Å)	44.874(4)
c (Å)	42.074(5)
α (°)	90.00
β (°)	90.00
γ (°)	120.00
V (Å ³)	73373(13)
T (K)	173 (2)
Z	18
F(000)	12564
R_{int}	0.0845
R_1 ($I > 2\sigma(I)$)	0.1337
w R_2 (all reflections)	0.2307

InOF denotes Indium-Organic Framework; More details see CIF files.

S2. Additional X-ray Crystal Structural Figures

asymmetric unit



[In(CO₂)₄] nodes

Figure S1. Asymmetric unit and coordination environment for BTB³⁻ ligands and In(III) centres in InOF-9, respectively.

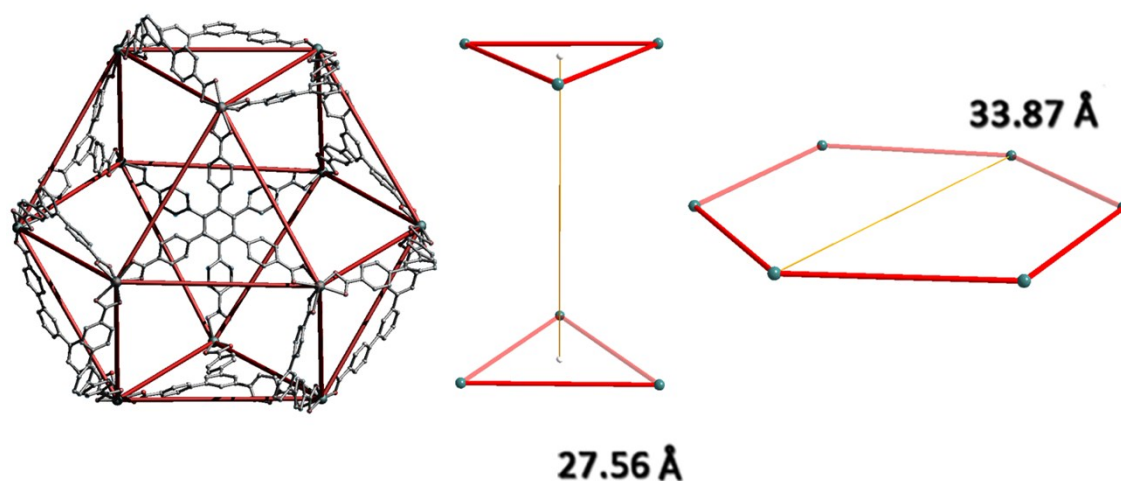


Figure S2. The dimensions of the extra-large cuboctahedron-based InOF-9.

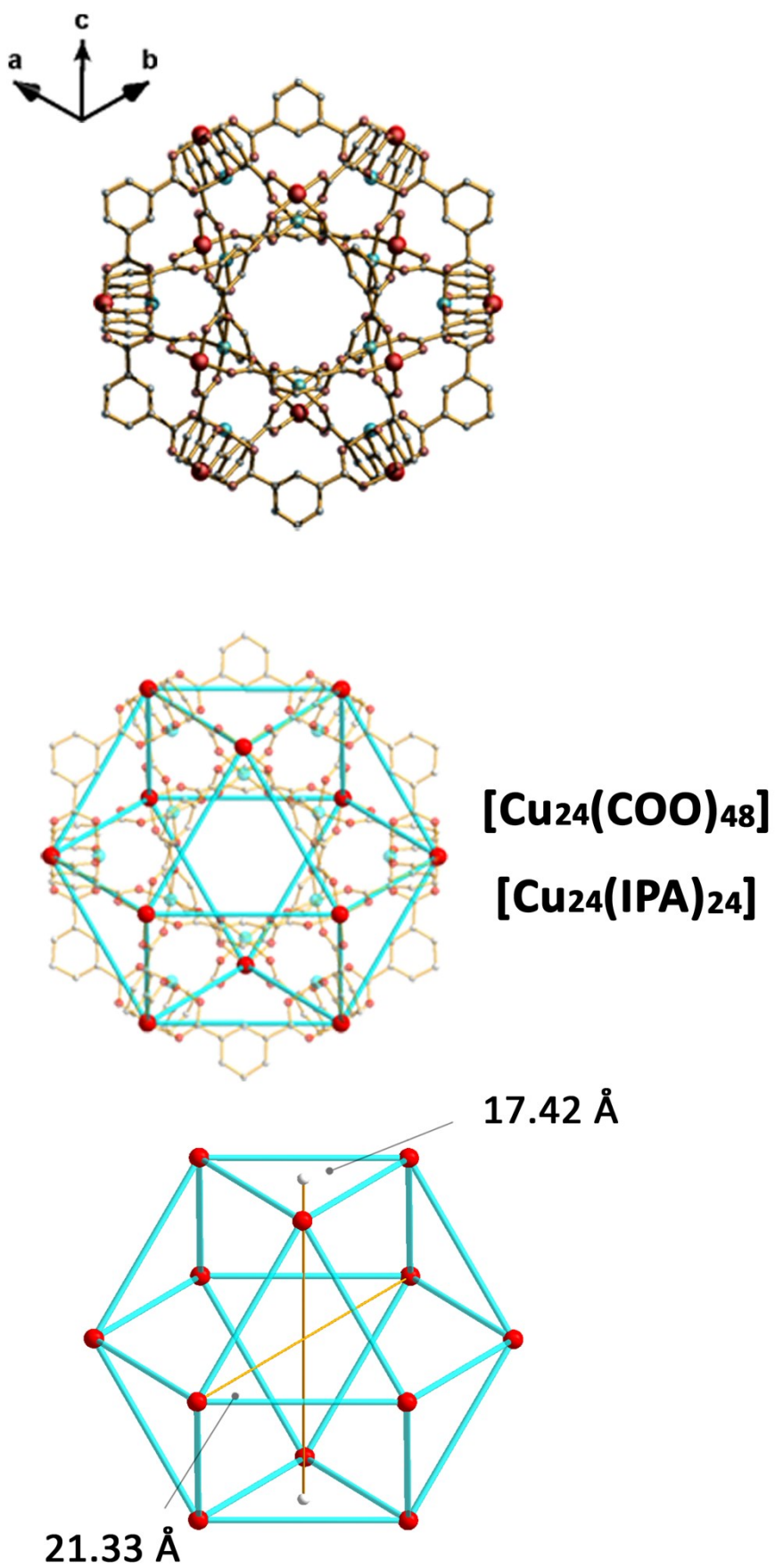


Figure S3. The structures and topological counterpart for Cu-IPA.

S3. Topological Analysis Results by TOPOS 4.0

1:C72 H40 In2 O16 (InOF-9)

#####

Topology for **BTB1**

Atom **BTB1** links by bridge ligands and has

Common vertex with					R(A-A)	
In 1	0.2399	0.1893	0.4600	(1 1 0)	9.829A	1
In 1	-0.1893	0.0506	0.4600	(-1 0 0)	9.829A	1
In 1	-0.0506	-0.2399	0.4600	(0-1 0)	9.829A	1

Topology for **BTB2**

Atom **BTB2** links by bridge ligands and has

Common vertex with					R(A-A)	
In 1	0.6160	1.0934	0.7933	(0 0 0)	9.804A	1
In 2	0.7603	0.8169	0.8029	(1 1 0)	9.820A	1
In 1	0.8107	1.0506	0.4600	(0 1 0)	9.866A	1

Topology for **BTB3**

Atom **BTB3** links by bridge ligands and has

Common vertex with					R(A-A)	
In 2	0.8497	0.2767	0.1363	(0 0 0)	9.784A	1
In 1	0.8107	0.0506	0.4600	(0 0 0)	9.816A	1
In 2	1.0936	0.4836	0.4696	(1 1 0)	9.854A	1

Topology for **BTB4**

Atom **BTB4** links by bridge ligands and has

Common vertex with					R(A-A)	
In 2	0.7233	0.5731	0.1363	(1 0 0)	9.746A	1
In 2	0.8497	0.2767	0.1363	(0 0 0)	9.746A	1
In 2	0.4269	0.1503	0.1363	(1 1 0)	9.746A	1

Topology for **In1**

Atom **In1** links by bridge ligands and has

Common vertex with					R(A-A)	
BTB 2	0.5898	-0.0630	0.3474	(0 0-1)	9.804A	1
BTB 3	0.9231	0.2763	0.3552	(0 0 0)	9.816A	1
BTB 1	1.0000	0.0000	0.4596	(1 0 0)	9.829A	1

BTB 2 0.7297 -0.0138 0.6808 (0-1 0) 9.866A 1

Topology for **In2**

Atom **In2** links by bridge ligands and has

Common vertex with					R(A-A)	
BTB 4	0.6667	0.3333	0.1454	(0 0 0)	9.746A	1
BTB 3	0.9231	0.2763	0.3552	(0 0 0)	9.784A	1
BTB 2	0.6805	0.0768	0.0141	(1 0-1)	9.820A	1
BTB 3	1.0571	0.3135	0.0218	(1-1-1)	9.854A	1

Structural group analysis

Structural group No 1

Structure consists of 3D framework with In3BTB4

There are 2 interpenetrating nets

FISE: Full interpenetration symmetry elements

Coordination sequences

BTB1: 1 2 3 4 5 6 7 8 9 10
 Num 3 9 18 37 42 88 93 149 147 250
 Cum 4 13 31 68 110 198 291 440 587 837

BTB2: 1 2 3 4 5 6 7 8 9 10
 Num 3 9 16 38 48 87 91 159 156 254
 Cum 4 13 29 67 115 202 293 452 608 862

BTB3: 1 2 3 4 5 6 7 8 9 10
 Num 3 9 17 39 47 90 95 162 157 256
 Cum 4 13 30 69 116 206 301 463 620 876

BTB4: 1 2 3 4 5 6 7 8 9 10
 Num 3 9 18 40 48 91 93 158 159 256
 Cum 4 13 31 71 119 210 303 461 620 876

In1: 1 2 3 4 5 6 7 8 9 10
 Num 4 8 22 31 62 68 122 123 205 195

Cum 5 13 35 66 128 196 318 441 646 841

In2: 1 2 3 4 5 6 7 8 9 10

Num 4 8 23 31 63 72 126 125 210 199

Cum 5 13 36 67 130 202 328 453 663 862

TD10=859

Vertex symbols for selected sublattice

BTB1 Point (Schlafli) symbol: $\{8^3\}$

Extended point symbol: $[8(4).8(4).8(4)]$

BTB2 Point (Schlafli) symbol: $\{6^2.8\}$

Extended point symbol: $[6.6.8(5)]$

BTB3 Point (Schlafli) symbol: $\{6.8^2\}$

Extended point symbol: $[6.8(4).8(4)]$

BTB4 Point (Schlafli) symbol: $\{8^3\}$

Extended point symbol: $[8(5).8(5).8(5)]$

In1 Point (Schlafli) symbol: $\{6^2.8^4\}$

Extended point symbol: $[6.8(3).6.8(3).8(2).8(2)]$

In2 Point (Schlafli) symbol: $\{6.8^5\}$

Extended point symbol: $[6.8(2).8(3).8(3).8(3).8(5)]$

Point (Schlafli) symbol for net: $\{6.8^2\}3\{6.8^5\}3\{6^2.8^4\}3\{6^2.8\}3\{8^3\}2$

3,3,3,3,4,4-c net with stoichiometry $(3-c)(3-c)3(3-c)3(3-c)(4-c)3(4-c)3$; 6-nodal net

New topology

S4. PXRD and TGA data

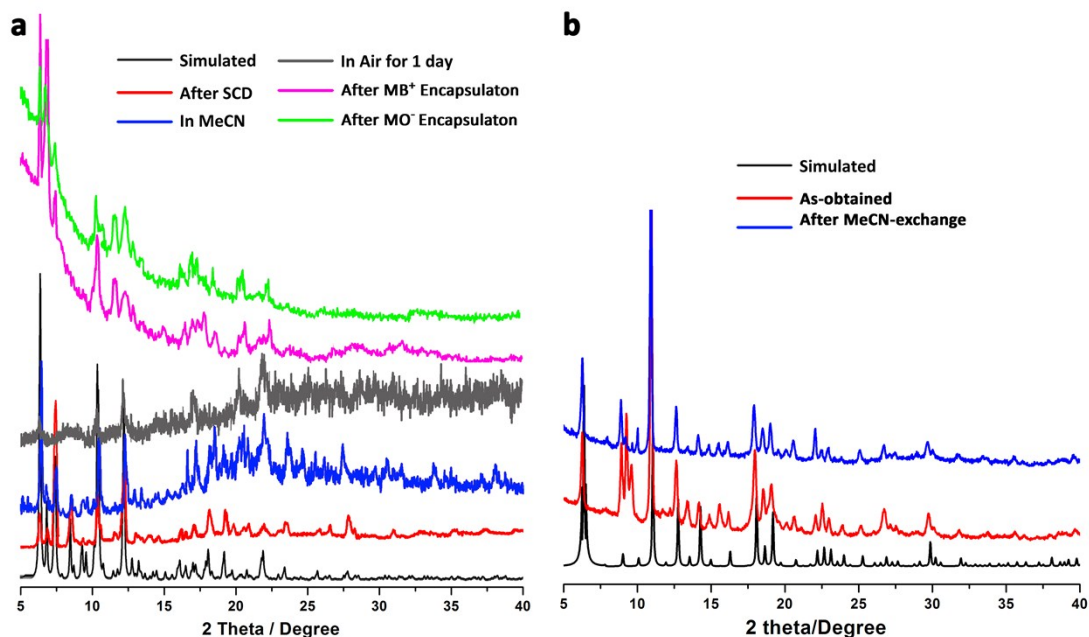


Figure S4. PXRD patterns of two crystalline materials used in the manuscript: For **InOF-9** (a): simulated from the crystallographic information file (black); from the SCD-activated sample (red); from the MeCN-exchanged sample (blue); exposed to air (grey); after MB⁺ exchange process (pink); after MO⁻ exchange process (green); For **Cu-IPA** (b): simulated from the crystallographic information file (black); from the as-prepared sample (red); from the MeCN-exchanged sample (blue).

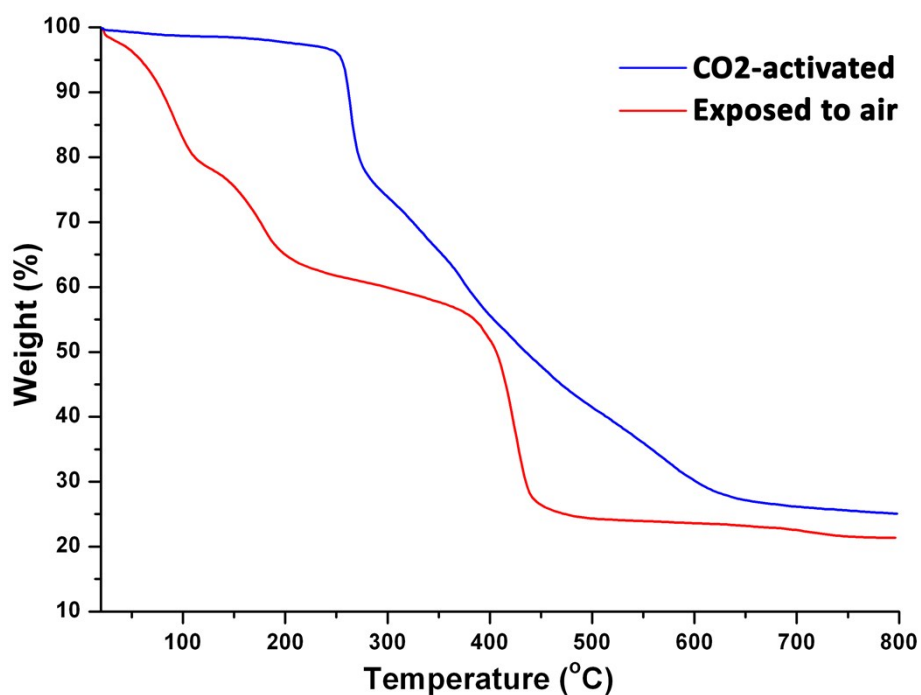


Figure S5. TGA curves for **InOF9** before and after supercritical CO₂ activation process.

S5. SEM and EDS

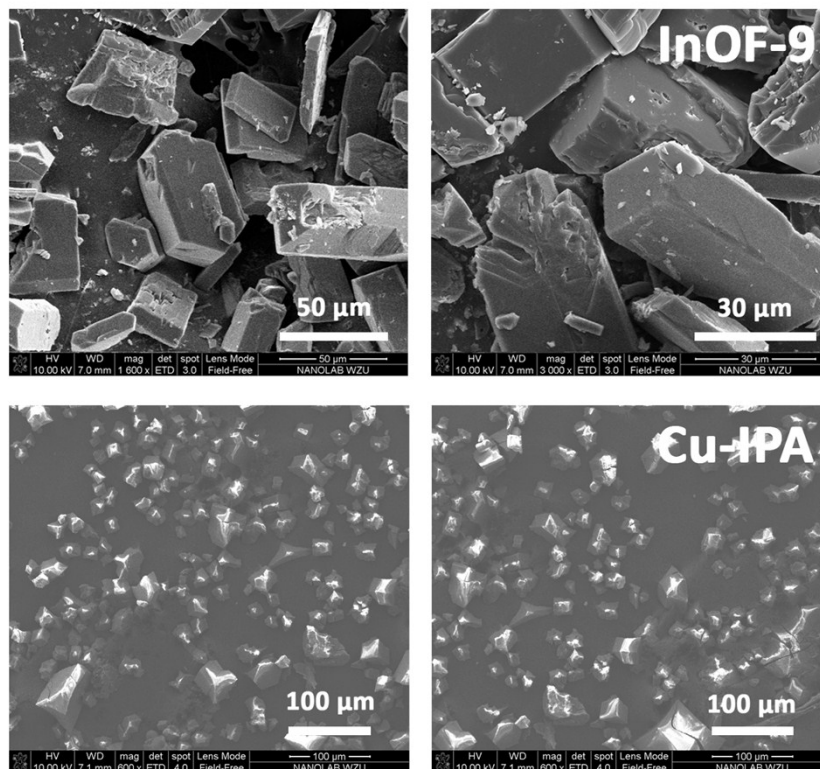


Figure S6. SEM images for InOF-9 (top) and Cu-IPA (bottom), respectively.

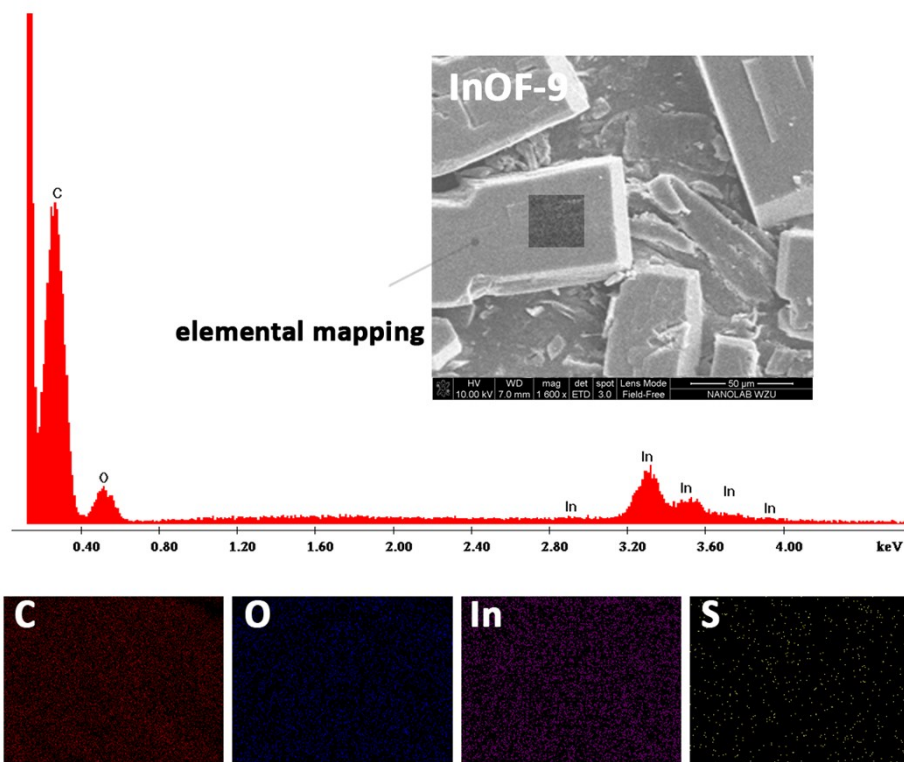


Figure S7. EDS and elemental mapping for as-prepared InOF-9 which show no evidence of sulfur element.

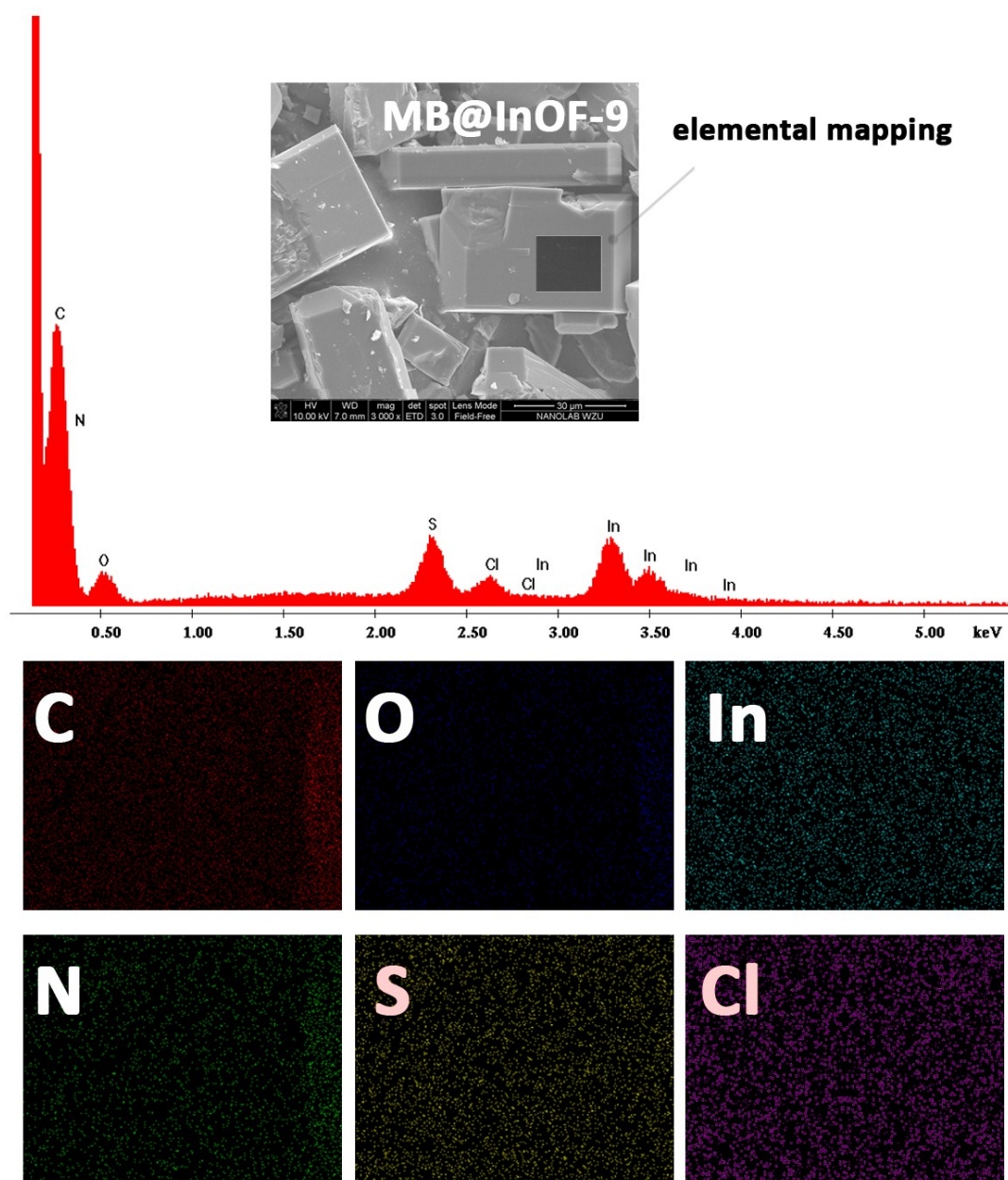


Figure S8. EDS and elemental mapping for MB-encapsulated **InOF-9** (**MB@InOF-9**), which indicate the effective accommodation of MB^+ molecules into the extra-large cavity with the evidence of the abundance of S and Cl elements from methylene blue molecules, which cannot be desorbed after adding excess of LiNO_3 salt into acetonitrile solvent.

S6. Dye Adsorption Peak Area and Percentage

To evaluate the accessibility of dyes to the voids of the frameworks, we take various dye molecules of different charge with similar sizes (methylene blue (MB^+ ; $4.78 \text{ \AA} \times 8.48 \text{ \AA} \times 17.24 \text{ \AA}$), methyl orange (MO^- ; $5.31 \text{ \AA} \times 7.25 \text{ \AA} \times 17.394 \text{ \AA}$), acid methyl red (MR)).

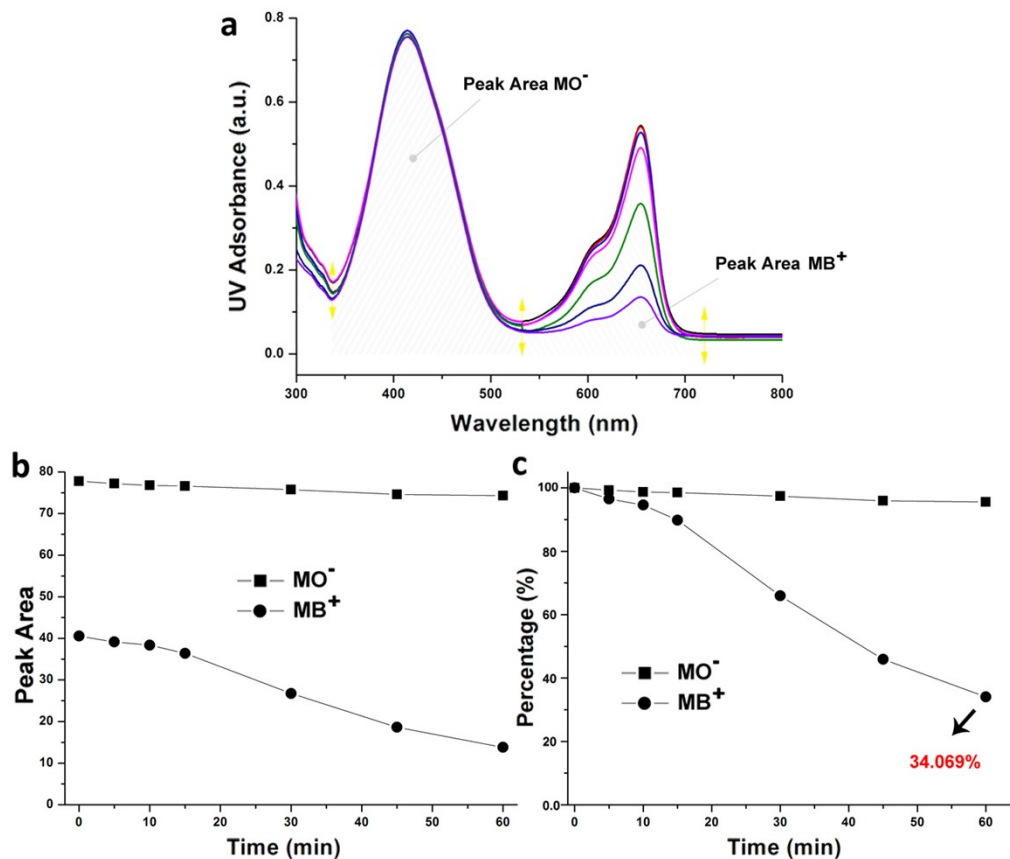


Figure S9. Peak area and percentage of mixing acetonitrile solvent of MB^+ and MO^- for InOF-9 in the selective dye sorption experiment.

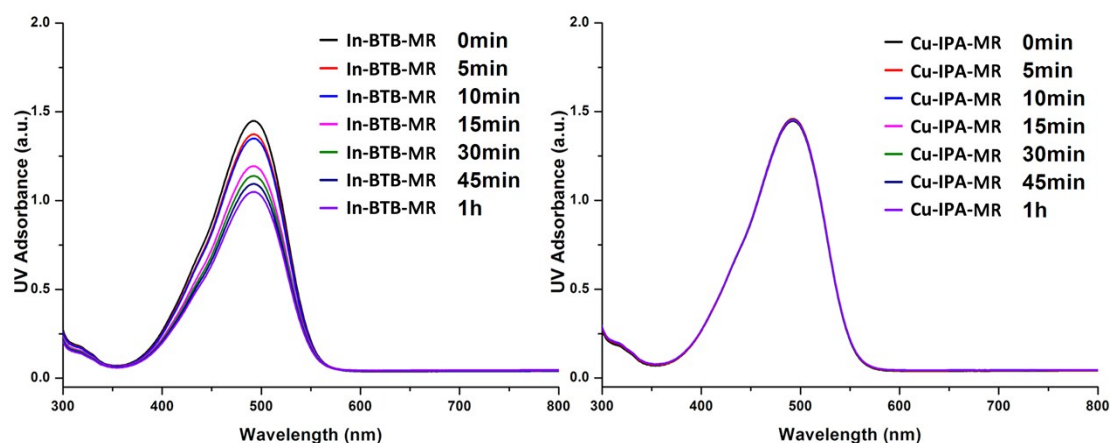


Figure S10. The electrically neutral MR dye molecule adsorption in 1 hour for InOF-9 and Cu-IPA, respectively.

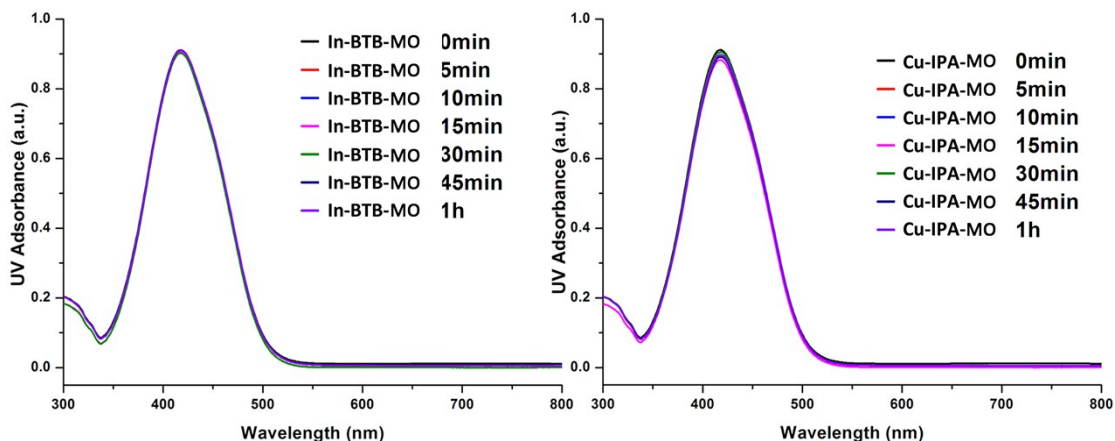


Figure S11. The electrically positive MO⁺ dye molecule adsorption in 1 hour for **InOF-9** and **Cu-IPA**, respectively.

We have tried by two methods you provided:

1. The relatively gentle method is to put the **MB@InOF-9** in the MeCN under 85 °C atmosphere for 1 day. Unfortunately, we still cannot detect the signal of released MB⁺ molecules by UV-vis (Yellow).
2. The relatively fierce method is to simultaneously add 0.1 mL HCl and 0.1 mL HNO₃ into the **MB@InOF-9**. Only by this way is the crystalline framework severely destroyed and the MB⁺ molecules could be released, but not completely. Absolutely, the UV-vis curves can easily be observed as well as the colour of solution after the strong acid inclusion (Dark Yellow to Dark Oyan). What should be mentioned here is that the crystalline materials turn to be powder immediately once the hydrochloric acid and nitrate acid are dropped.

The UV-vis with these two methods is concluded by the following figure below:

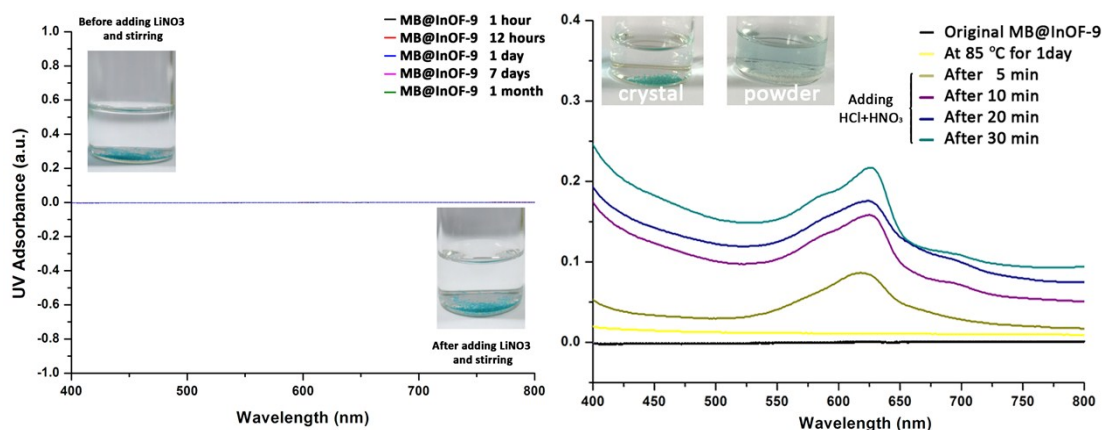


Figure S12. (Left) The dye release experiment for **MB@InOF-9**. The colour of **MB@InOF-9** is clear and unchanged, and the UV-vis curves don't detect the peak of MB⁺ molecules. (Right) The failure of release by high temperature, while to decompose the framework with strong acid with unlocking the encapsulated MB⁺ successfully.

S7. Sorption Analyses.

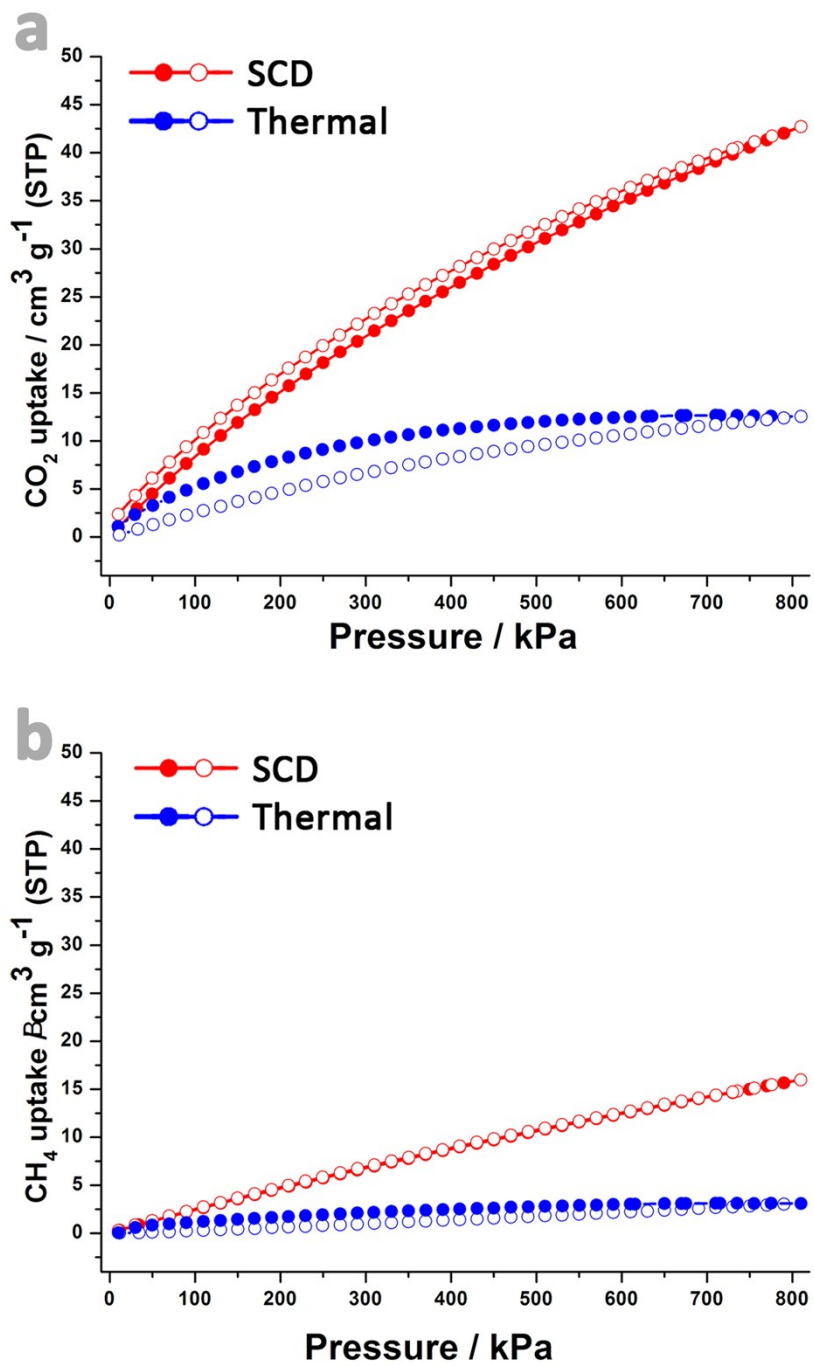


Figure S13. Methane and carbon dioxide sorption experiment at 295 K activated by SCD drying (in red) and thermal treatment (in Blue).

S8. Proposed Entrapped MB⁺ Route

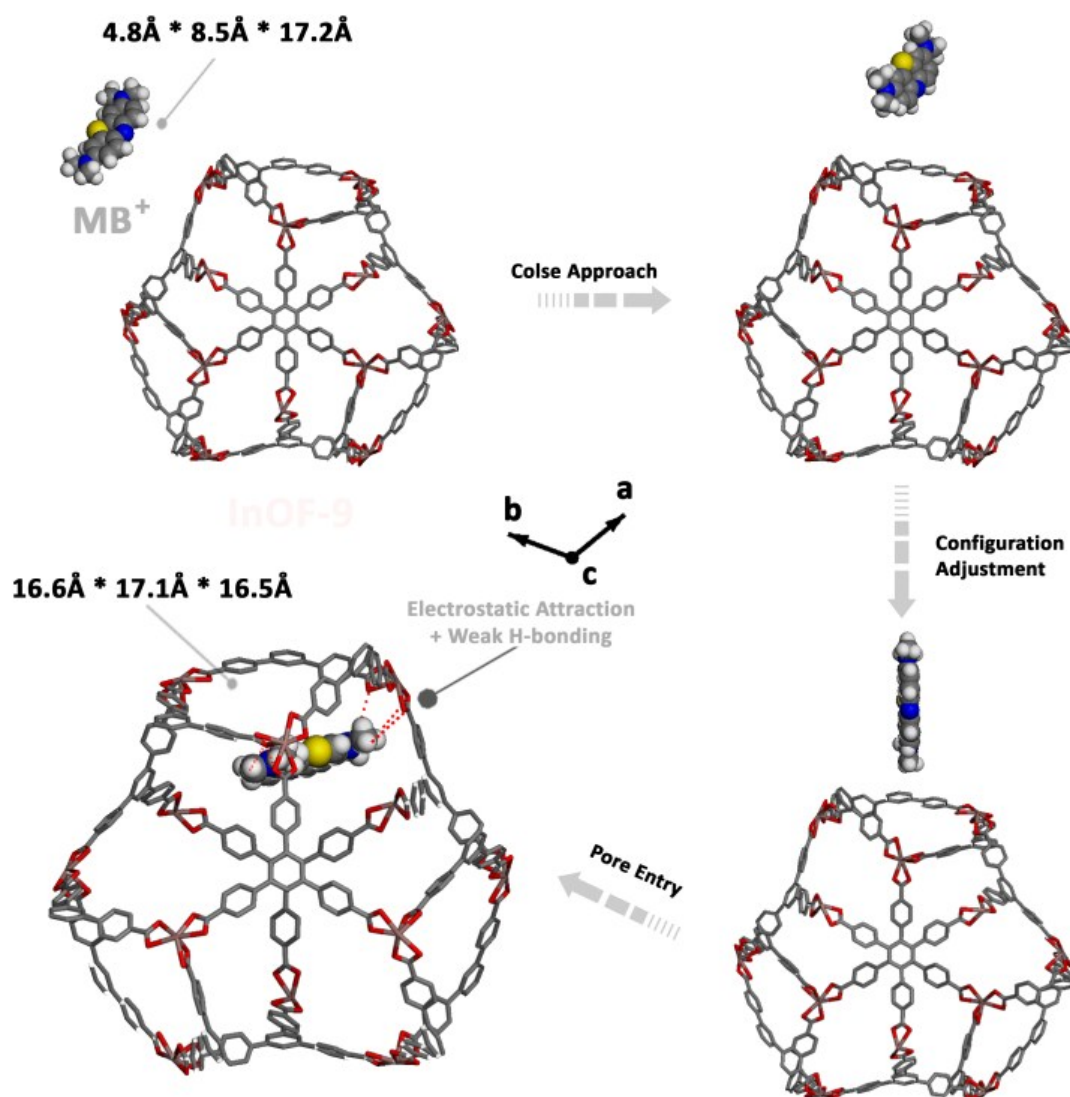


Figure. S14. The proposed mechanism on the entry for dye MB⁺ molecules: Step 1, approach to surface (top left); Step 2, move to windows (top right); Step 3, adjust its configuration (down left); Step 4, trapped inside (down right).

The release test is subsequently conducted on MB@InOF-9 that exhibits surprisingly no desorption of MB⁺ dye molecule, even after 1 month with adding excess LiNO₃ and stirring at the speed of 600 round min⁻¹ (Fig. S12). As the failure of releasing dye molecules for MB@InOF-9, we want to elucidate the possibility of MB⁺ molecule immobilization inside the large cuboctahedron owing to intense electrostatic forces between the host framework and guest dye molecules. Therefore, a conjecturable mechanism is theoretically proposed by Materials Studio: Step 1, one

planar MB⁺ molecule approaches close to the external surface far from a long distance by attraction; Step 2, the small MB⁺ molecule moves very close to In-based trigonal windows (shown above) and/or tetragonal windows; Step 3, it will adjust the configuration to the optimal situation and then penetrate the windows; Step 4, finally, it will be trapped inside of extra-large cuboctahedron by electrostatic attraction together with weak hydrogen bonding interactions, which cannot be destroyed by adding the excess of small inorganic LiNO₃ salt in order to release the MB⁺ molecules from the cuboctahedron.^{S6}

S9. References.

- [S1] O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, *J. Appl. Cryst.* **2009**, *42*, 339.
- [S2] SHELXS, G.M. Sheldrick, *Acta Cryst.* **2008**, *A64*, 112.
- [S3] SHELXL, G.M. Sheldrick, *Acta Cryst.* **2008**, *A64*, 112.
- [S4] (a) A. L. Spek, *J. Appl. Crystallogr.* **2003**, *36*, 7; (b) P. v.d. Sluis and A. L. Spek, *Acta Crystallogr., Sect. A*, **1990**, *46*, 194.
- [S5] A. P. Nelson, O. K. Farha, K. L. Mulfort, J. T. Hupp, *J. Am. Chem. Soc.*, **2009**, *131*, 458-460.
- [S6] Y. Chen, V. Lykourinou, C. Vetromile, T. Hoang, L. J. Ming, R. W. Larsen, S. Q. Ma, *J. Am. Chem. Soc.*, **2012**, *134*, 13188-13191.